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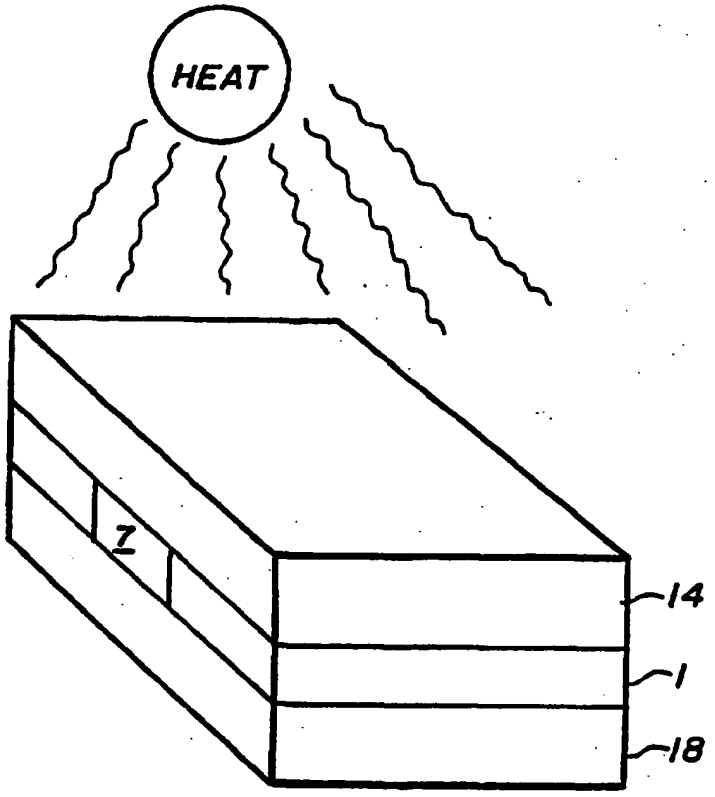
(54) Title: DIFFUSION CONTROL METHOD FOR IMPROVED PHOTOPOLYMER OPTICAL WAVEGUIDES

(57) Abstract

Optical waveguide devices for interconnecting optical fibers and use in integrated optical systems are disclosed. The invention includes a substantially dry method for making the devices and intermediate elements, including an intermediate waiting step to allow diffusion of the chemical components across layer boundaries, thus providing control over the resulting refractive index profiles of the devices.



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TITLE

DIFFUSION CONTROL METHOD FOR IMPROVED PHOTOPOLYMER OPTICAL WAVEGUIDES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to optical waveguide devices, elements for making the devices and methods of making the devices and elements. The devices are for interconnecting optical fibers, optical components and modules and for use in integrated optical systems.

2. Description of the Prior Art

In optical communication systems, messages are transmitted by carrier waves of optical frequencies that are generated by sources such as lasers or light-emitting diodes. There is much current interest in such optical communication systems because they offer several advantages over conventional communication systems, such as having a greatly increased number of channels of communication and the ability to use other materials besides expensive copper cables for transmitting messages. One such means for conducting or guiding waves of optical frequencies from one point to another is called an optical waveguide. The operation of an optical waveguide is based on the fact that when a medium which is transparent to light is surrounded or otherwise bounded by another medium having a lower refractive index, light introduced along the inner medium's axis is highly reflected at the boundary with the surrounding medium, thus, producing a guiding effect. The most frequently used material for such a waveguide device is glass, which is formed into a fiber of specified dimensions.

As the development of optical circuits proceeded, it became necessary to have devices which could couple, divide, switch and modulate the optical waves from one waveguide fiber to another.

Some optical fibers are interconnected by other optical fibers cut to length. These devices have only two terminals-one at each end. Photohardened films containing a waveguide have been proposed for this use, such as in U.S. Patent No. 3,809,732. However, the device disclosed therein cannot be easily coupled to and aligned with an optical fiber. Further, due to the uneven surface of its film, one cannot easily protect its exposed surface from the environment.

Another method used to form an optical coupling device involves the application of standard photolithographic processes and diffusion. By this prior art process, standard lithographic processes are used to define a pattern in a photoresist layer deposited on a chosen substrate. Then, an etchant is applied to etch the photoresist-defined pattern into the substrate. Next, a metal is deposited in the etched region by vacuum deposition. The photoresist pattern is then lifted off with an appropriate solvent, carrying with it unwanted metal deposits. The structure is then heated to diffuse the metal deposited in the etched region into the substrate, to form a waveguiding layer therein. See, for instance, U.S. Patent No. 4,609,252. In addition to the fact that many steps are involved in such a process, there is also a limitation on the thickness of the metal which may be deposited. First, since vacuum deposition is a relatively slow process, there is the limitation of the excessive amount of time required to deposit a thick layer of metal. Secondly, as more and

more metal is deposited, new centers for deposition are created, resulting in an uneven deposit.

To form branches, two or more fibers have been bonded to a common optical port using an adhesive having an index of refraction closely matched to that of the fibers. The fibers are very small in diameter and must be handled with extreme care, bundled together for strength, and attached to a support at intervals. Fabrication of the equivalent of a printed circuit board comprised of these discrete fibers and optical devices is labor-intensive, expensive, slow, tedious, and not readily adapted to automated fabrication techniques. Another method used to form such a coupler is to fuse or melt fibers together so that light from one fiber can pass to the connected fibers. However, in such a fusion process it is difficult to control the extent of fusion and the exact geometry and reproducability of the final structure.

A device of particular interest is the "Y-coupler", which is a "y"-shaped device that couples signals together or divides them apart. "Y"-shaped devices have been made in a wet process by exposing a liquid photoactive layer to ultraviolet radiation through a mask. Then a solvent is used to remove the unpolymerized portions of the layer. See, for instance, U.S. Patent No. 4,609,252. The waveguide of this device, like those mentioned above, isn't protected from the environment or readily coupled to an optical fiber. Further, being a wet process, it has the tendency of being messy and the problem of disposing of the spent solvent.

Another "Y"-shaped coupler device is disclosed in U.S. Patent No. 4,666,236. It further discloses a

device with one input branch and three output branches. These devices are also made by a wet process exposing a liquid photopolymer film to light to create a waveguide. The unexposed liquid film is dried and becomes part of the device. The film is further coated with a layer, such as an acrylic resin, to prevent deposition of dust and staining. Again, this process is wet and, thus, inherently messy.

U.S. Patent No. 3,809,686 shows waveguides created in a single photopolymer film by focusing a beam of light within the film and moving the film. It shows multiple waveguides in a single film. In one embodiment, the waveguides exhibit evanescent coupling of light between the waveguides. It further teaches the creation and use of holographic diffraction gratings as light couplers. However, it is difficult to focus light within a film to form a homogenous waveguide with clear and distinct boundaries.

An object of this invention is to provide an improved method of forming conductors of light for interconnecting optical components and modules. These light conductors may be formed with a plurality of branches and terminals.

SUMMARY OF THE INVENTION

The general purpose of this invention is to provide new and improved optical waveguide structures having predetermined geometry and to provide the process for forming these structures, which possess most, if not all, of the advantages of the prior art devices and processes while alleviating their significant disadvantages discussed above.

In order to accomplish the above-described general purpose of this invention, the present invention comprises a substantially dry method of

making an optical waveguide device with at least one buried channel waveguide in a laminated and hardened matrix. The steps include:

exposing to light at least a first region of a substantially dry photohardenable film having first and second surfaces, with a support removably adhered to the first surface, polymerizing at least one monomer in the film and changing the refractive index in the region to form at least a first optical waveguide;

laminating a first surface of a first substantially dry photohardenable layer to the film second surface, with a support removably adhered to a second surface of the first layer;

removing the support from the film first surface;

laminating a first surface of a second substantially dry photohardenable layer to the film first surface, with a support removably adhered to a second surface of the second layer; and

hardening the layers and film forming a hardened matrix, substantially fixing the indexes of refraction of the layers and the film, and creating at least one buried waveguide.

Applicants have discovered that it can be advantageous to employ an additional step, after the final laminating step, comprising waiting a predetermined period of time, typically in the interval from five to forty-five minutes, to allow for inter-layer diffusion of the chemical components of the buffer layers and the waveguide film so that the refractive index profile of the waveguide can be controlled. It is desirable to maintain the entire apparatus at a temperature below that at which

hardening would occur. This temperature will affect the rate of the diffusion process. For single mode guiding the preferred embodiment comprises having a relatively uniform index profile running perpendicular to the parallel planes of the layered structure. Additionally, such diffusion can occur in the unhardened regions of the waveguide film. This improved method of refractive index profile control provides the waveguide designer with more flexibility in construction of high efficiency photopolymer optical waveguides. The ensuing hardening step can be accomplished either by thermal hardening or photohardening as previously described.

BRIEF DESCRIPTION OF THE DRAWING

The invention may be more fully understood from the following detailed description thereof taken in connection with accompanying drawings which form a part of this application and in which:

Figure 1 is a perspective view of a photohardenable film removably adhered to a support.

Figure 2a is a schematic representation of a first embodiment for forming an optical waveguide element comprising a waveguide in a film on a support.

Figure 2b is a schematic representation of a second embodiment for forming an optical waveguide element comprising a waveguide in a film on a support.

Figure 2c is a schematic representation of a third embodiment for forming an optical waveguide element comprising a waveguide in a film on a support.

Figure 3 depicts an optional step of flooding the film having a waveguide on a support with light resulting in an element.

Figure 4 shows a laminated element comprising from top to bottom a support, a photohardenable layer, a film having a waveguide, and another support.

Figure 5 illustrates an optional step of flooding the element of Figure 4 with light.

Figure 6 is the element of Figure 4 or 5 with one of the supports removed.

Figure 7 is a perspective view of an optical waveguide element comprising from top to bottom a support, a photohardenable or photohardened layer, a film having a waveguide, a photohardenable layer, and a support.

Figure 8 shows the step of hardening the element of Figure 7 by flooding it with light.

Figure 9 shows the step of hardening the element of Figure 7 or the device of Figure 8 by heating it.

Figure 10 is a perspective view of an optical waveguide device for use in integrated optical systems, the device comprising from top to bottom a first hardened layer, a hardened film having a waveguide, and a second hardened layer.

Figure 11 shows the step of stabilizing the element of Figure 10 by heating it.

Figure 12 shows a buried channel waveguide device coupled to an optical fiber with light being injected through the fiber and waveguide.

Figure 13a illustrates directing coherent light within the element of Figure 4 to produce a holographic diffraction grating.

Figure 13b is a cross sectional representation of a holographically formed grating coupling light to a waveguide buried between layers.

Figure 14 is a cross sectional view of a laminated device having a film, multiple layers, an end support, waveguides and a grating.

Figure 15 is a reproduction of a photograph of the near-field view of the output of the waveguide of a 1 x 1 device formed using a wait time of about zero (0) minutes.

Figure 16 is a reproduction of a photograph of the near-field view of the output of the waveguide of a 1 x 1 device formed using a wait time of about fifteen (15) minutes.

Figure 17 is a reproduction of a photograph of the near-field view of the output of the waveguide of a 1 x 1 device formed using a wait time of about forty-five (45) minutes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Throughout the following detailed description, similar reference numerals refer to similar elements in all Figures of the drawings.

Referring to Figure 1, an element used in the method of the present invention is illustrated comprising a substantially dry photohardenable film 1 removably adhered to a support 2. The film 1 has a first surface 3 and a second surface 4. The support similarly has a first surface 5 and a second surface 6. The first surface 5 of the support 2 is removably adhered to the first surface 3 of the film 1. In a preferred embodiment, the surfaces 3, 4, 5 and 6 of the film 1 and the support 2 are substantially flat.

The film 1 may have a thickness in the range of 2 micrometers through 15 micrometers or above, preferably in the range of 4.5 micrometers through 8.0 micrometers, and more preferably about 5.3 micrometers.

The first step of the method of the present invention comprises exposing to light at least a first region 7 of the film 1 polymerizing at least one monomer in the film 1 and changing the refractive index of the region 7 to form at least a first optical waveguide. The term waveguide is defined by those skilled in this art to include the entire area that transmits radiant energy. This technically includes some area just around the exposed region. However, for simplicity, the exposed region can be considered to substantially be the waveguide. In theory, the waveguide formation is believed to be due to a self-focusing property of the film material. Upon exposure to light, a polymerization reaction is induced in the exposed region. It is believed that there is interdiffusion between the exposed and unexposed regions, at least near the interface of these regions. This interdiffusion changes the refractive index of the exposed region creating a lens-like exposed region directing the light in a self focused fashion to create a narrow smooth walled waveguide of approximately the same dimension as the mask area or light beam width. Three embodiments for performing this first step are illustrated in Figures 2a, 2b and 2c.

In Figure 2a, a focused laser light source 8 exposes the region 7 to form the waveguide. A translational mechanism 9 is connected to the laser light source 8 and/or the support 2 for moving the laser light source 8, the support 2 or both, to create the waveguide having a desired and/or predetermined pattern. Here, the exposed region 7 has a substantially elongated box configuration having an optical axis 10 through the longitudinal center of the

region 7. A physical cross section of the exposed region 7 perpendicular to the optical axis 10 is substantially rectangular. On both sides of the region 7 are remaining unexposed regions 11 of the film 1.

Figure 2b shows an alternate embodiment for exposing a region 7'. Here, a non-focused laser light source 8' is generally directing actinic radiation toward the element of Figure 1. An opaque mask 12 is positioned between the laser light source 8' and the film 1, typically contacting and covering the second film surface 4. The mask 12 has at least a patterned area 13 therein through which actinic radiation from the light source 8' exposes region 7'. The patterned area can have any desired configuration, including the substantially Y configuration shown in Figure 2b. Exposing the region 7' through this area 13 results in the creation of a waveguide having a substantially Y configuration. Described more generically, the region can have one end adapted to inlet or outlet light connected to a plurality of ends (e.g., 2, 3, 4...) adapted to inlet or outlet light. As in the Figure 2a embodiment, there are remaining unexposed regions 11' in the film 1.

A third embodiment for performing the exposing step of the present method is illustrated in Figure 2c. Here, actinic radiation from a light source 8'' exposes a first region 7'' and a second region 7''' of the film 1 through an opaque mask 12'. This mask 12' has first and second areas 13' and 13'' for the light to pass through exposing regions 7'' and 7''', respectively. The second area 13'' approaches and is in part parallel to the first area 13'. Thus, after exposure, the exposed second region 7''' and the

corresponding waveguide approaches and is in part parallel to the exposed first region 7'' and the corresponding waveguide. As a result, the waveguides can be positioned to exhibit evanescent coupling of light injected into one of the waveguides by gradually leaking or coupling the injected light into the other waveguide.

In each of these preferred embodiments, after exposure, the first and second surfaces 3 and 4 of the film 1 remain substantially flat. This facilitates subsequent laminating of layers on the film surfaces. As such, Figures 2a, 2b and 2c illustrate the making of optical waveguide elements in accordance with this invention useful in making optical waveguide devices which in turn are useful in integrated optical systems.

Figure 3 illustrates an optional step which follows the exposing step. The element resulting from the exposure step can be flooded with light, such as broadband ultraviolet light. This polymerizes some of at least one monomer in the film and typically most or all of one or all of the monomers in the film. This may allow for easy removal or attachment of the support 2. This resulting optical waveguide element can similarly be used in making optical waveguide devices in accordance with the method of this invention.

Next, referring to Figure 4, a first substantially dry photohardenable layer 14 is laminated to the second film surface 4. The first layer 14 has first and second surfaces 15 and 16, respectively. The first layer 14 first surface 15 is laminated to the second film surface 4 by placing them in intimate contact and controllably applying pressure with rollers to remove air between the film 1 and

layer 14. The first layer 14 is tacky. If the optional flooding step illustrated in Figure 3 is not performed, then the film 1 is also tacky. Thus, the film 1 and first layer 14 easily adhere to one another. A support 17 is removably adhered to the second surface 16 of the first layer 14. Figure 4 illustrates another optical waveguide element in accordance with the present invention useful in making optical waveguide devices.

Figure 5 shows an optional flooding step similar to that illustrated in Figure 3, except the element being flooded is modified as described in relation to Figure 4. The element resulting from the first laminating step can be flooded with light, such as broadband ultraviolet light. This polymerizes some of at least one monomer (and typically most or all of one or all of the monomers) in the first layer 14 and further polymerizes some of the at least one monomer in the film 1 (if not already polymerized by a previous flooding step). Extensive crosslinking or polymerization occurs between the monomer(s) of the layer 14 adjacent to the monomer(s) of the film 1 forming a diffuse boundary line or region. The resulting optical waveguide element is also useful in making an optical waveguide device in accordance with this invention.

Figure 6 shows the element after the next step of removing the support 2 from the film 1 first surface 3.

Then, referring to Figure 7, a second substantially dry photohardenable layer 18 is laminated to the film 1 first surface 3. The second layer 18 has first and second surfaces 19 and 20, respectively. The second layer 18 first surface 19 is

laminated to the film first surface 3 by placing them in intimate contact and controllably applying pressure with rollers removing air between the film 1 and the second layer 8. The second layer surfaces 19 and 20 are tacky and, thus, easily adhere to the film 1. A support 21 is removably adhered to the second layer second surface 20. Another optical waveguide element results which is useful in making optical waveguide devices.

Figure 8 illustrates a step of hardening the element depicted in Figure 7 by flooding it with light, such as broadband ultraviolet light. Throughout this application, the term "broadband ultraviolet light" means light in the spectral region of about 350 through 400 nanometers. This step occurs for minutes, preferably 5, but can last longer. If this is the first flooding step, then this is the first polymerization of at least one monomer (and typically most or all of one or all monomers) in the remaining regions 11 in the film 1 and the first and second layers 14 and 18, respectively. It further polymerizes the at least one monomer in the region 7 of the film 1. If this is not the first flooding step, it polymerizes at least one monomer in the second layer and continues polymerizing the at least one monomer in the rest of the element. Some crosslinking or polymerization occurs between the previously polymerized film 1 and the monomer(s) in the second layer 18 forming a boundary line or region that is more evident than if the film 1 had not previously been flooded with light. A device results having at least one buried channel waveguide in a laminated and photohardened matrix useful in integrated optical systems.

Figure 9 illustrates another possible step of hardening the element depicted in Figure 7 by heating it. Actually, the layers and film can be heated before, in combination with, after, or in lieu of the light flooding step to harden or further harden the device. This heating step occurs at a temperature in the range of about 50°C through 200°C and preferably in the range of about 100°C through 150°C for a duration of minutes, preferably 5.

Photohardenable compositions are typically less sensitive to temperatures up to 100°C than above 100°C. However, hardening may be initiated as low as 50°C if held at the temperature for a sufficient period of time. As the temperature is increased beyond 100°C, thermally initiated hardening increases significantly.

Applicants have discovered that it can be advantageous to employ an additional step after lamination of the first buffer layers 14 and 18 directly on the waveguide film 1, which has only been exposed image-wise in the waveguide region 7. The added step is a predetermined wait period at a predetermined temperature to allow for inter-layer diffusion of the chemical components of the buffer layers 14 and 18 and the waveguide film 1, so that the refractive index profile and magnitude of the waveguide 7 relative to the waveguide film 1 and buffer layers 14 and 18 can be controlled. For single-mode guiding the preferred embodiment for waveguide 7 comprises having a relatively uniform, nearly step-like to parabolic-like index profile running perpendicular to the parallel planes of the layered structure formed by layers 14 and 18.

Control of both the length of the predetermined wait period and the temperature at which the waveguide device is held during this period can be used to control the waveguiding properties of waveguide 7. While the predetermined wait period may depend on temperature, an interval of about 5 to 45 minutes is typically required. In general, longer wait periods do not markedly alter the waveguiding properties of waveguide 7. During the predetermined wait period, it is desirable to maintain the entire apparatus at a temperature at or above ordinary room temperature but below that at which hardening would occur. It is preferred that the optional flooding step illustrated in Figure 3, carried out before lamination of the first buffer layer 14, and the optional flooding step illustrated in Figure 5, carried out after the first buffer layer 14 has been laminated to waveguide film 1, be omitted. In this fashion diffusion into the waveguide film 1 may occur from both waveguide layers 14 and 18.

Additionally, during the predetermined wait period such diffusion can occur between the unhardened regions of waveguide film 1 and buffer layers 14 and 18. This facilitates control of the refractive index of waveguide 7 relative to that of waveguide film 1; enhances the ultimate strength and uniformity of the bonding at the interface of waveguide 1 and buffer layers 14 and 18; and modifies the final properties of the waveguide film 1, such as hardness as a function of temperature, due to the diffusion of crosslinking monomers into waveguide film 1 from buffer layers 14 and 18. The ensuing hardening step can be accomplished either by thermal hardening or photohardening, as previously described. This

improved method of refractive index profile control provides the waveguide designer with more flexibility in construction of high-efficiency photopolymer optical waveguides.

After the hardening step, a maximum refractive index increase in the localized waveguide region as measured by an AUSJENA Interphako microscope occurs in the film 1 in the range of 0.001 through 0.40 measured at 546 nanometers wavelength. The localized refractive index increase, Δn, for the purposes of this invention, is derived by conventional shearing interference microscopy techniques and is calculated assuming a uniform index shift through the film such that Δn is effectively an average using the following equations:

$$f\lambda = \Delta d$$

$$f = \frac{a}{b}$$

$$\frac{a\lambda}{b} = \Delta d$$

where d = assumed waveguide thickness, typically the film thickness

a = waveguide fringe shift

b = fringe spacing

λ = 0.546 μ wavelength of light in the microscope.

This localized refractive index increase is not to be confused with a refractive index modulation measured from gratings prepared holographically, as described by Kogelnik (H. Kogelnik, Bell Syst. Tech. J., 48, 2909-2947, 1969).

After the hardening step, the waveguide is transparent in the range of 0.6 through 1.6 micrometers wavelength. It is effectively transparent at 1.3 micrometers for single mode operation.

Also after the hardening step, the maximum refractive index of the matrix except in and near the waveguide is in the range of 1.45 through 1.60 measured at 632 nanometers depending on formulation and/or extent of interlayer diffusion from adjoining layers or film of different indexes. The refractive index is determined by using an ABBE refractometer manufactured by Karl Zeiss.

The supports 17 and 21 can be removed from the device resulting from the hardening step as shown in Figure 10.

It has been found that a time delay of 5 to 120 minutes, preferably 20 to 30 minutes, after each flooding step and before removal of support sheets and/or subsequent lamination is also desirable to facilitate interlayer diffusion and polymerization.

Figure 11 shows an optional, but preferred, step of stabilizing the device shown in Figure 10 by heating it, typically after the hardening step. This heating step similarly occurs at a temperature in the range of about 50°C through 200°C and preferably in the range of about 100°C through 150°C. However, this stabilizing step occurs longer than the hardening step. Preferably the stabilizing step occurs in the range of about 30 minutes through 2 hours and more preferably for about an hour. This heating makes the device more environmentall- stable ensuring water and other elements in the environment will not interfere with proper operation of the device. Further, this heating provides thermal stabilization of optical and

mechanical properties allowing operation of the resulting device over a wide range of temperatures without modification of the device properties.

In the device of Figure 10 or 11, the first and second layers 14 and 18, respectively, have equal thicknesses. Further, the remaining regions 11 are equal in size and symetric on either side of region 7. As such, the device has a buried channel waveguide that can be dimensioned to easily couple to virtually any optical fiber. Figure 12 shows the device of either Figure 10 or 11 coupled to an optical fiber 22. The fiber has a cylindrical core 23 and a cylindrical cladding 24 surrounding the core 23. Standard single mode fiber has a cladding diameter of about 125 microns and a core diameter of about 7 microns. The laminated waveguide device, now clad from above and below, is shown advantageously coupled to the optical fiber 22 simply by abutting the fiber core 23 to the buried waveguide aligning their optical axes. This is accomplished by merely positioning the optical waveguide device adjacent the optical fiber on a flat surface, if the dimensions of the device are preselected for the particular fiber. This aligning can be facilitated by using a film 1 having a thickness which substantially defines one dimension of a substantially rectangular cross section of the waveguide. For coupling to standard single mode fiber, the film thickness should be about 5 to 6 micrometers, preferably 5.3; the exposure width should be about 5 microns; and each one of the first and second layers should be about 59.85 micrometers thick. The total matrix thickness can be made any dimension including about 125, 180 and 200 micrometers.

Figure 12 also shows the step of injecting light from a light source 25 into and through the optical fiber 22 and buried waveguide.

Figure 13a illustrates an optional step of directing at least two coherent light beams, such as from lasers 26 and 27 to intersect in an area within the element of Figure 4. These beams are directed to provide a resultant light intensity that spatially varies in such a way as to produce a holographic diffraction grating 28. The grating comprises regions of varying refractive index for input of light to the waveguide or waveguide portion or output of light from the waveguide or waveguide portion. A grating can direct light to or from a waveguide in the film or to or from one of the layers or from a waveguide or waveguide portion in the film (or one of the layers) to another waveguide or waveguide portion within the film (or the one layer). Further, as well known in the art, gratings can be wavelength selective by only directing one or more predetermined wavelengths. Figure 13b shows a cross section of the Figure 10 or 11 device having the holographic diffraction grating 28 in the first layer 14 and the region 7. The grating 28 can be in areas selected from the group consisting of at least part of the region, at least part of one of the layers near the region, and combinations thereof, provided that there has been no previous hardening step for the film and/or layer in which the grating is to be constructed. Further, the directing step can be accomplished at other stages of development of the device described herein.

One of the advantages of the present invention is the ease of adding one or more substantially dry photohardenable or photohardened layers with or

without a waveguide or grating. This versatility is demonstrated in the device illustrated in Figure 14. This optical waveguide device has exposed regions 7, 29, 31 and 33 in film 1 and layers 14, 30 and 35, respectively. It further shows buffer layers 18, 32, 34 and 36, and a support 21. Region 7 has a holographic diffraction grating to direct light from region 7 to region 29 or the reverse. As an alternative to using a grating to change the direction of light, layer 30 illustrates other techniques, such as one disclosed in U.S. Patent No. 4,472,020, are possible. Further, the break between layers 34 and 36 is intended to show that devices can have as many or few layers as desired. Of course, waveguides in different layers or in the film and a layer could be formed to exhibit evanescent coupling therebetween.

All layers including those designated by the numbers 14, 18, 30, 32, 34, 35 and 36 can be made out of the same material as the film. Then the hardened device matrix is substantially homogenous in composition and refractive index except in and near the waveguide. Preferably, however, after the hardening step, the waveguide has a refractive index about 0.005 to 0.060 greater than the hardened film and about 0.001 to 0.025 greater than the hardened layers. Of course, regardless of whether different materials are used for different layers and the film, the composition and refractive index in each exposed region is substantially homogenous in composition and refractive index.

The photohardenable film and layers used herein are thermoplastic compositions which upon exposure to actinic radiation form crosslinks or polymers of higher molecular weight to change the refractive index

and rhelogical character of the composition(s). Preferred photohardenable materials are photopolymerizable compositions, such as disclosed in U.S. Patent 3,658,526. In these materials, free radical addition polymerization and crosslinking of a compound containing one or more ethylenically unsaturated groups, usually in a terminal position, hardens and insolublizes the composition.

While the photopolymerizable film or layer is a solid sheet of uniform thickness it is composed of three major components: a solid, solvent soluble, preformed polymeric material known as the binder; at least one liquid ethylenically unsaturated monomer capable of addition polymerization to produce a polymeric material; and a photoinitiator system activatable by actinic radiation. Although the film or layer is solid composition, components interdiffuse before, during and after imaging exposure until they are fixed by the hardening step. Interdiffusion may be further promoted by incorporation into the composition of an otherwise inactive plasticizer. In addition to the liquid monomer, the composition may contain solid monomer components capable of interdiffusing in the solid composition and reacting with the liquid monomer to form a copolymer.

In the preferred compositions for use as the film or layers in this invention, the binder and the liquid monomer are selected so that the monomer contains one or more moieties taken from the group consisting essentially of substituted or unsubstituted phenyl, phenoxy, biphenyl, naphthyl, naphthyloxy, and heteroaromatic groups containing one to three aromatic rings; chlorine; and bromine, and the binder is substantially free of the specified moieties. The

monomer contains at least one such moiety and may contain two or more of the same or different moieties of the group, provided the monomer remains liquid. Contemplated as equivalent to the groups are substituted groups where the substitution may be lower alkyl, alkoxy, hydroxy, cyano, carboxy, carbonyl, amino, amido, imido or combinations thereof provided the monomer remains liquid and diffusable in the photopolymerizable layer.

Preferred liquid monomers are 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, phenol ethoxylate acrylate, 1-(p-chloro phenoxy) ethyl acrylate, p-chlorophenyl acrylate, phenyl acrylate, 1-phenylethyl acrylate, and 2-(2-naphthyloxy)ethyl acrylate. While monomers useful in this invention are liquids, they may be used in admixture with a second solid monomer of the same type, e.g., N-vinyl-carbozle.

The solvent soluble polymeric material, or binder, is substantially free of phenyl, phenoxy, biphenyl, naphthyl, naphthyloxy, heteroaromatic group containing one to three aromatic rings, chlorine, and bromine.

Preferred binders are cellulose acetate butyrate polymers; acrylic polymers and inter polymers, such as polymethyl methacrylate; polyvinylacetate; copolymers of vinyl acetate with tetrafluoroethylene and/or hexafluoropropylene; polyvinyl acetal; polyvinyl butyral; polyvinyl formal; as well as mixtures thereof.

The photoinitiator system may contain a photoinitiator and, if desired, a sensitizer which extends the spectral response into the near ultraviolet and visible spectral regions.

Preferred photoinitiators include CDM-HABI, i.e., 2-(o-chlorophenyl)-4,5-bis(m-methoxyphenyl)-imidazole dimer; o-Cl-HABI, i.e., 1,1'-biimidazole, 2,2'-bis(o-chlorophenyl)-4,4', 5,5'-tetraphenyl-; and TCTM-HABI, i.e., 1H-imidazole, 2,5-bis(o-chlorophenyl)-4-(3,4-dimethoxyphenyl-), dimer each of which is typically used with a hydrogen donor, e.g., 2-mercapto benzoxazole or 4-methyl-4H-1,2,4-triazole-3-thiol (MMT). MMT is preferred for compositions containing N-vinyl carbazole. Ketones, such as benzophenone, Michler's ketone, and ethyl Michler's ketone, can also be used as sensitizers, with or without HABI.

Useful sensitizers which extend spectral response into the visible include the following:

DEAW, i.e., Cyclopentanone, 2,5-bis-((4-(diethylamino)-phenyl)methylene); and

Dimethoxy-JDI, i.e., 1H-Inden-1-one, 2,3-dihydro-5,6-dimethoxy-2-((2,3,6,7-tetra-hydro-1H,5H-benzo[i,j]quinolizin-9-yl)-methylene)-.

Nonionic surfactants may be added to the photopolymerizable composition as coating aids. Preferred coating aids are polyethylene oxide, such as Polyox® WSRN-3000 and Polyox® WSR-205, and fluorinated nonionic surfactants, such as Fluorad® FC-430.

Other components in addition to those described above can be present in the photopolymerizable compositions in varying amounts. Such components include: plasticizers, optical brighteners, ultraviolet radiation absorbing material, thermal stabilizers, and release agents.

Amounts of ingredients in the photopolymerizable compositions will generally be within the following percentage ranges based on total weight of the

photopolymerizable layer: monomer(s), 5-60%, preferably 15-50%; initiator system, 0.1-10%, preferably 1-5%; binder, 25-90%, preferably 45-75%; plasticizer, 0-25%, preferably 0-15%; other ingredients 0-5%, typically 1-4%.

The supports can be any substance transparent to actinic radiation that provides sufficient support to handle the combined film 1 and layer 2. Preferably the support 2 is transparent to light in the spectral region of 0.6 through 1.6 micrometers wavelengths. The term "support" is meant to include natural or synthetic supports, preferably one which is capable of existing in a flexible or rigid film or sheet form. For example, the support or substrate could be a sheet or film of synthetic organic resin, or a composite of two or more materials. Specific substrates include polyethylene terephthalate film, e.g., resin-subbed polyethylene terephthalate film, flame or electrostatic discharge treated polyethylene terephthalate film; glass; cellulose acetate film; and the like. The thickness of the supports has no particular importance so long as it adequately supports the film or layer removeably adhered to it. A support thickness of about 25 to 50 micrometers using polyethylene terephthalate provides sufficient rigidity to a film 6 microns thick.

The following examples are provided as an illustration of, but do not limit, the invention.

EXAMPLE 1

A substantially dry photohardenable waveguide film of about 5.3 μm thick, having the ingredients listed in Table I, coated on a 25 μm thick clear polyethylene terephthalate support, in approximately a

10 cm X 13 cm section, is exposed to broad band ultraviolet light in the spectral range of 350 to 400 nm through a conventional chrome-plated glass photo-mask to produce a 1 X 4 (one waveguide end to four waveguide ends or four to one) coupler waveguide pattern. After exposure and then an appropriate delay time of about 15 minutes, the mask is removed.

Next, a first substantially dry photohardenable buffer layer of about 30 μm thick, having the ingredients listed in Table II, coated on a 25 μm thick clear polyethylene terephthalate support, is laminated to the film surface over the waveguide pattern as shown in Figure 4. .The resultant element is subsequently flooded with broadband ultraviolet light. The film support is then removed by mechanical stripping.

Next, a second photohardenable buffer layer of identical composition and structure, as the first buffer layer, with support, is laminated to the opposite surface of the waveguide film and flooded as above.

In subsequent steps, the supports attached to the buffer layers are removed. Sequentially, a third and fourth buffer layer of identical composition and structure as the first buffer layer are laminated to the first and second buffer layers, respectively, with flooding between each lamination and subsequent removal of the buffer layer support to form an optical waveguide device having a buried channel waveguide.

The resultant device is heated at 100°C for 60 minutes to achieve thermal stability.

The indexes of refraction of the film and layers in the laminated device were determined and are listed in Table III.

TABLE I

FILM

Ingredient	Weight %
Cellulose acetate butyrate, Eastman CAB 531-1	56.54
2-Phenoxyethyl acrylate (POEA)	35.00
Triethyleneglycol dicaprylate (TDC)	5.00
2-Mercaptobenzoxazole (MBO)	1.89
o-Cl-HABI	1.00
Sensitizing dye (DEAW)[1]	0.56
2,6-Di-tert-butyl-4-methylphenol (BHT)	0.01

[1]2,5-Bis([4-(diethylamino)-phenyl]methylene)cyclopentanone

TABLE II

BUFFER LAYER[1]

Ingredient	Weight %
CAB[1] 381-20	45.49
POEA[2]	20.00
N-Vinylcarazole (NVC)	15.00
Ethoxylated bisphenol A diacrylate, Sartomer 349	15.00
o-Cl-HABI[3]	3.00
4-Methyl-4H-1,2,4-triazole-3-thiol (MMT)	1.50
BHT[4]	0.01

1 Cellulose acetate butyrate

2 2-Phenoxyethyl acrylate; CAS 48145-04-6

3 1,1'-Biimidazole, 2,2'-bis-O-chlorophenyl-4,4', 5,5'-tetraphenyl; CAS 1707-68-2

4 2,6-Di-tert-butyl-4-methylphenol

TABLE III

Layer or Film	REFRACTIVE INDEX
Active (non-exposed) Film	1.535
Waveguide Region of FIlm	1.566 Avg.
Buffer Layer No. 1	1.545
Buffer Layer No. 2	1.548
Buffer Layer No. 3	1.545
Buffer Layer No. 4	1.548

Examples 2-4 illustrate the effect of wait time on the refractive index profile of waveguide 7 and on the difference in refractive index between waveguide 7 and waveguide film 1 after the hardening step.

EXAMPLE 2

The compositions given in Table IV were extrusion die coated from 95:5 dichloromethane/ methanol at about 24% total solids onto a clear 50 micron thick polyethylene terephthalate support. (It should be understood that "total solids" refers to the total amount of nonvolatile material in the coating solution even though some of the additives may be nonvolatile liquids at ambient temperature.) The coatings were passed through a heated dryer and a 23 micron thick polyethylene terephthalate coversheet laminated to each coating as it emerged from the dryer.

TABLE IV

Ingredient[1]	Buffer Layer (% by weight)	Waveguide Film (% by weight)
CAB 531-1	54.83	55.40
Photomer® 4039[2]	33.28	34.94
Sartomer 349	4.75	5.00
MMT	1.90	1.90
o-Cl HABI	0.95	1.00
EMK[3]	0.48	---
Benzophenone	2.85	---
DEAW	---	0.55
BHT	---	0.01
Polyox® WSRN-3000[4]	---	1.0%
Polyox® WSR-205[5]	0.95%	---
FC-430[6]	---	0.20
Thickness	26.3 micrometers	7.1 micrometers

[1] See also Tables 1 and 2 for description of ingredients.

[2] Phenol ethoxylate monoacrylate; CAS 56641-05-5; Henkel Process Chemical Company.

[3] Ethyl Michler's ketone; 4,4'-bis(diethylamino)-benzophenone; CAS 90-93-7.

[4] Polyethylene oxide, MW 400,000; Union Carbide Corporation

[5] Polyethylene oxide, MW 600,000; Union Carbide Corporation.

[6] Fluorad® FC-430, liquid nonionic surfactant; fluoroaliphatic polymeric esters; CAS 11114-17-3; 3M Company.

A substantially dry photohardenable waveguide film 1, having the composition and thickness given in Table IV, in approximately 13 cm by 13 cm rectangular section, was exposed to 16 mJ/cm^2 of broad band ultraviolet light (350 to 400 nanometers) through a conventional crome-plated glass photo-mask which had been laminated to the film to produce a 9 micron wide, straight, 1 X 1 (one waveguide input end to one waveguide output end) waveguide. The film and laminated mask were heated on a hotplate to 38°C prior to exposure. After exposure the film and mask were held at 38°C for 5 minutes and the mask removed.

Next a substantially dry photohardenable buffer layer 14, having the composition and thickness given in Table IV, was laminated to the surface of waveguide layer 1. Then support 2 was stripped from the film as described in Example 1. Then a second substantially dry photohardenable buffer layer 18 was laminated to the free surface of waveguide layer 1. A first side of the laminated structure of buffer layer 14 with support 17, waveguide film 1, and buffer layer 18 with support 21 was immediately flooded wtih 2000 mJ/cm^2 of broad band ultraviolet light at 38°C. Flooding was repeated on the second side.

In subsequent steps, following the procedure of Example 1, the supports 18 and 21 attached to buffer layers 14 and 17 were removed and a third and fourth buffer layer added to form an optical waveguide device having buried channel waveguide 7. The resultant device was heated at about 92-95°C for about 60 minutes to achieve thermal stability.

EXAMPLE 3

The procedure of Example 2 was repeated except that the laminated structure consisting of buffer layer 14 with support 17, waveguide film 1, and buffer layer 18 with support 21 was held at about 24°C (i.e., room temperature) for 15 minutes and then flooded with broad band ultraviolet light at 38°C.

EXAMPLE 4

The procedure of Example 2 was repeated except that the laminated structure consisting of buffer layer 14 with support 17, waveguide film 1, and buffer layer 18 with support 21 was held at about 24°C (i.e., room temperature) for 45 minutes and then flooded with broad band ultraviolet light at 38°C.

The ends of the device including waveguide 7 were microtoned and a light source aligned and connected with one end of the waveguide 7 with an index matching liquid was positioned to provide maximum light intensity at the output end. Single mode 1550 nm wavelength light was introduced into one end of waveguide 7 from the light source. The light source was laser diode directed through a greater than 1 meter length of Corguide® SMF 28 (Corning Glass Works, Corning, NY) optical fiber. Light was collected from the other end of waveguide 7 with a Bausch and Lomb immersion lens with a numerical aperture of 1.3 using an index matching fluid (Cargille Series AA, 1.458, Cargille Labs, Inc., Cedar Grove, NJ). The light was captured with a Model C2741 Hamamatsu IR camera (Hamamatsu Photonic Systems, Bridgewater, NJ). The output was also analyzed by a Model 321 Colorado Video, Inc., vertical line scanner and the output of the vertical

line scanner displayed simultaneously on the video monitor.

Figures 15, 16 and 17 are reproductions of photographs of the near-field output of the waveguide generated in Examples 2, 3 and 4, respectively. They illustrate a non-uniform refractive index profile at a wait period of about zero minutes and progressively more uniform refractive index profiles as the wait period increases to about 45 minutes. (It should be understood that wait period refers to the time between the lamination of the buffer layers to the waveguide film and the hardening step and, consequently, does not include the about 2-5 minutes required for lamination.) The intensity profile of the output along the vertical line perpendicular to the layers (indicated by the vertical line near the center of the figure), is portrayed by the video cursor trace on the left side of the near-field image in each figure. This intensity profile is dependent upon the refractive index profile of waveguide 7. It is seen that in Figure 15, corresponding to a wait time of zero minutes, a bilobal intensity distribution is obtained. In Figures 16 and 17, corresponding to longer wait times, more uniform intensity distributions are observed.

The refractive index difference between waveguide 7 and waveguide film 1, as measured by an Interphako-Pol-D shearing interference microscope, was 0.010 for zero minutes, 0.009 for 15 minutes, and 0.007 for 45 minutes wait time, respectively, illustrating that wait time also affects the difference in refractive index between the waveguide 7 and the waveguide film 1.

Those skilled in the art, having the benefit of the teachings of the present invention as hereinabove

set forth, can effect numerous modifications thereto. These modifications are to be construed as being encompassed within the scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A substantially dry method of making an optical waveguide device with at least one buried channel waveguide in a laminated and hardened matrix, comprising the steps of:

exposing to light at least a first region of a substantially dry photohardenable film having first and second surfaces, with a support removably adhered to the first surface, polymerizing at least one monomer in the film and changing the refractive index of said first region to form at least a first optical waveguide;

laminating a first surface of a first substantially dry photohardenable layer to the film second surface, with a support removably adhered to a second surface of the first layer;

removing the support from the film first surface;

laminating a first surface of a second substantially dry photohardenable layer to the film first surface, with a support removably adhered to a second surface of the second layer;

allowing the laminated layers and film to stand for a predetermined wait period adequate to control the refractive index of said first region as desired; and

hardening the layers and film forming a hardened matrix, substantially fixing the indexes of refraction of the layers and the film, and forming at least one buried waveguide.

2. The method of Claim 1, wherein said wait period is at least five minutes.

3. The method of Claim 1, wherein said wait period is in the range of fifteen to forty-five minutes.

4. The method of Claim 1, wherein the hardening step comprises flooding the layers and film with light forming the hardened matrix.

5. The method of Claim 1, wherein the hardening step comprises heating the layers and film at a temperature in the range of about 50°C through 200°C for a duration of several minutes.

6. The method of Claim 1, wherein the temperature of said waveguide is maintained at or about room temperature during said wait period, but in any case at a temperature lower than that which would cause hardening of said photohardenable film and said photohardenable layers.

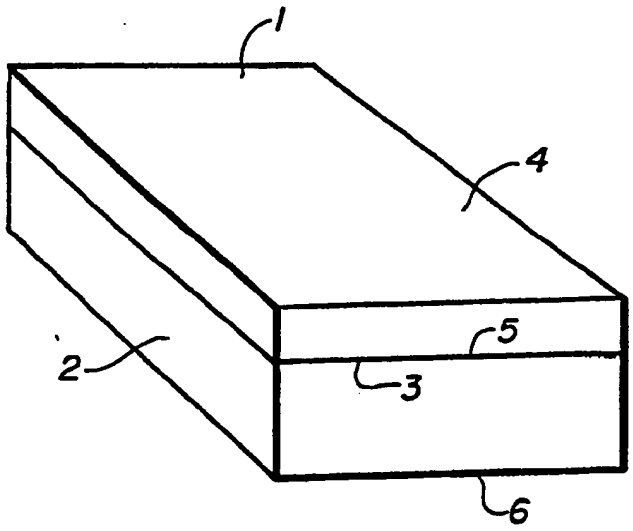


Fig. 1

Fig. 2a

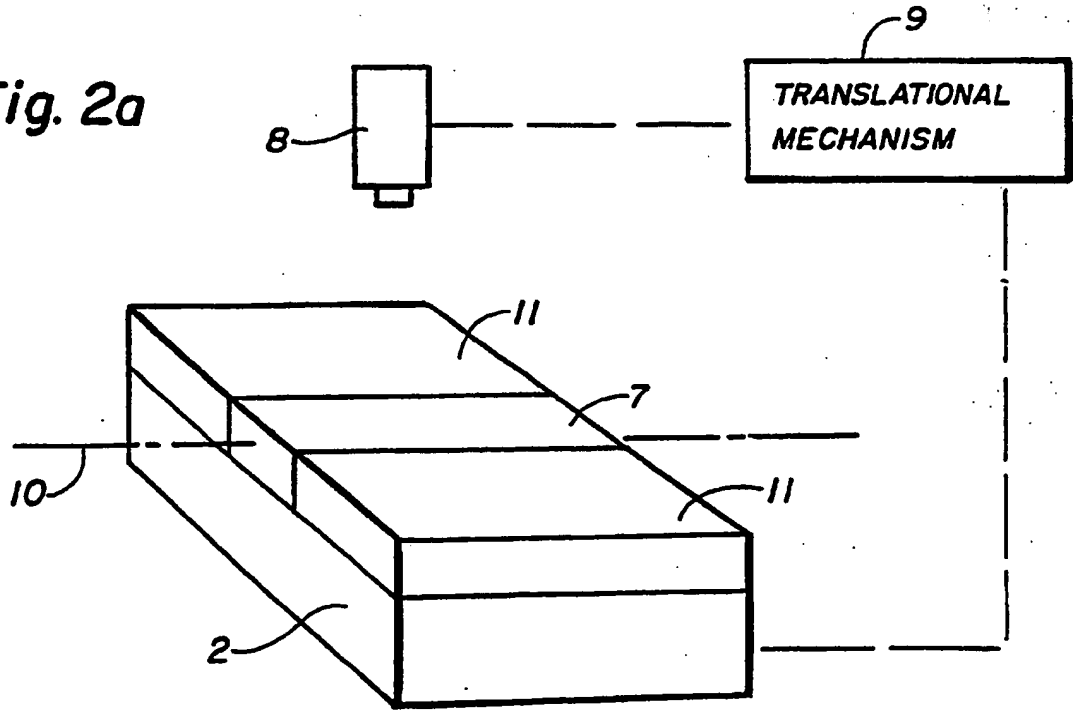


Fig. 2b

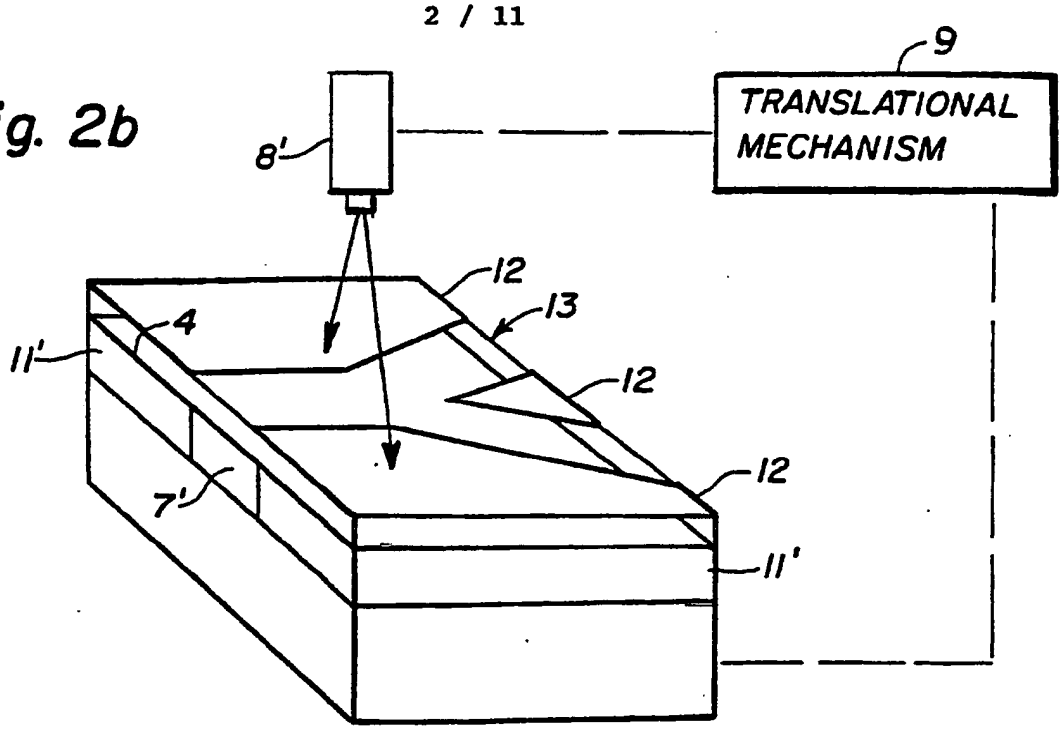


Fig. 2c

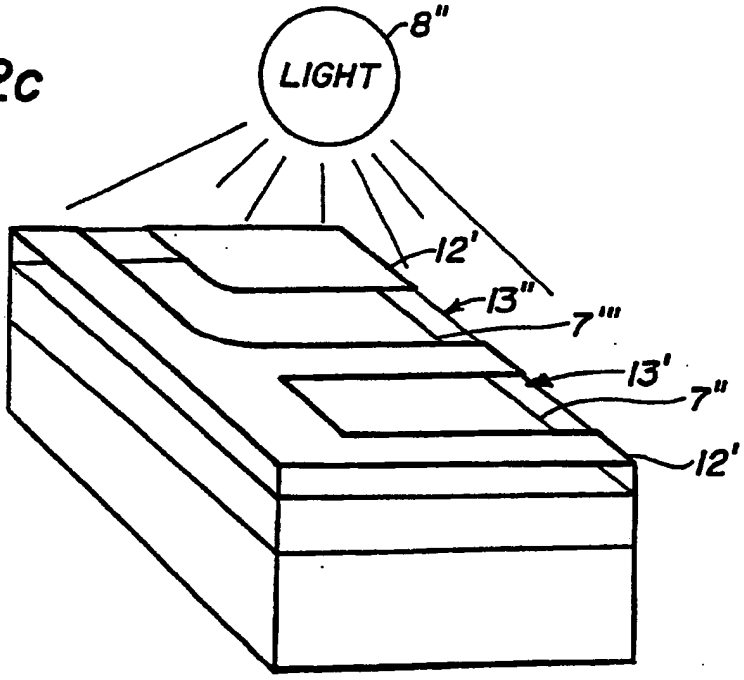


Fig. 3

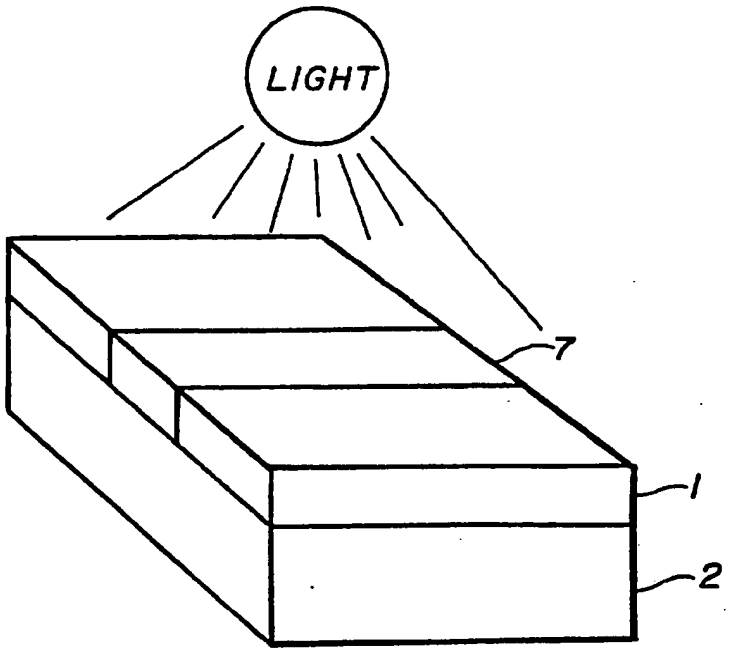


Fig. 4

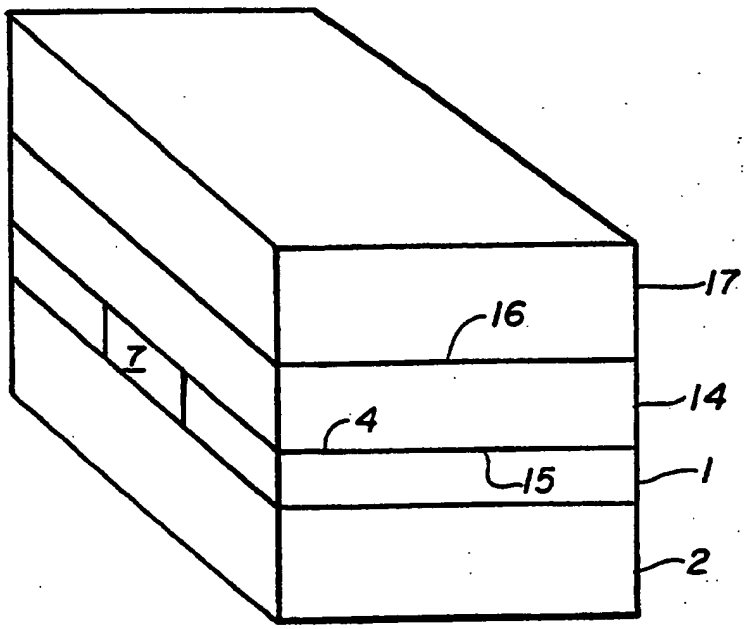


Fig. 5

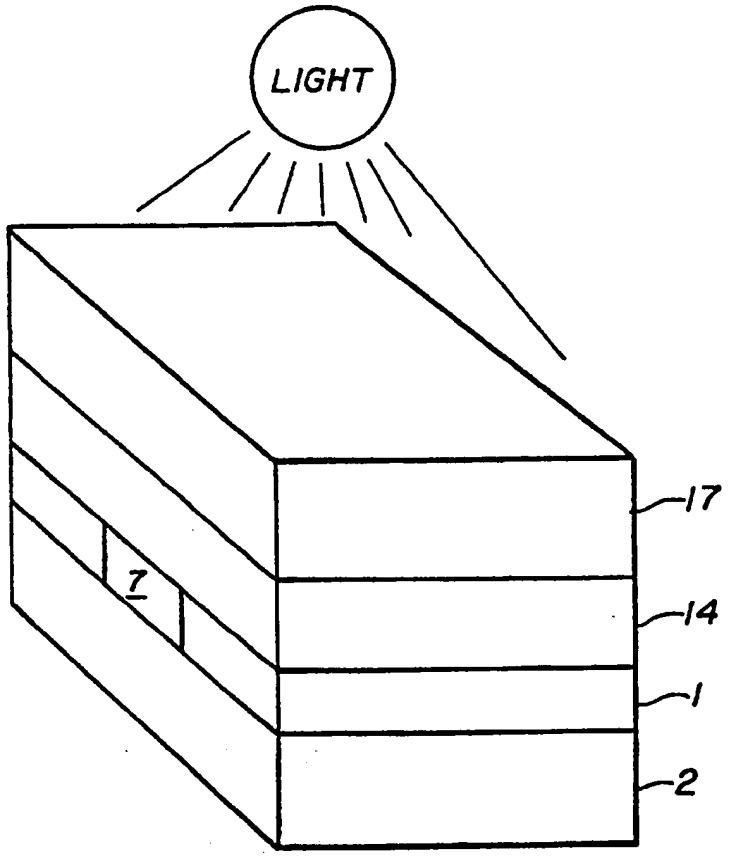


Fig. 6

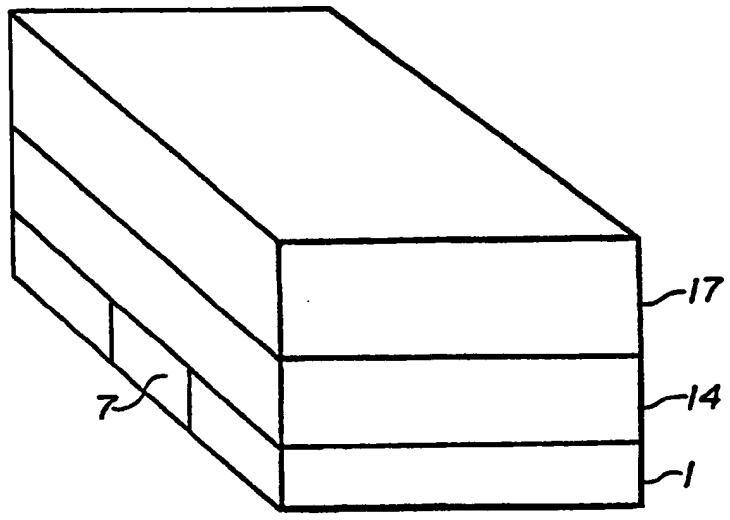


Fig. 7

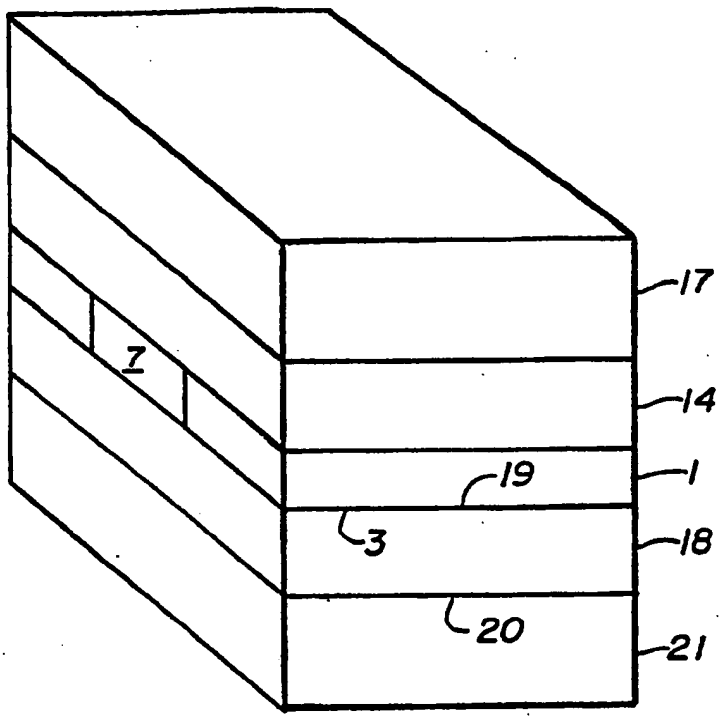


Fig. 8

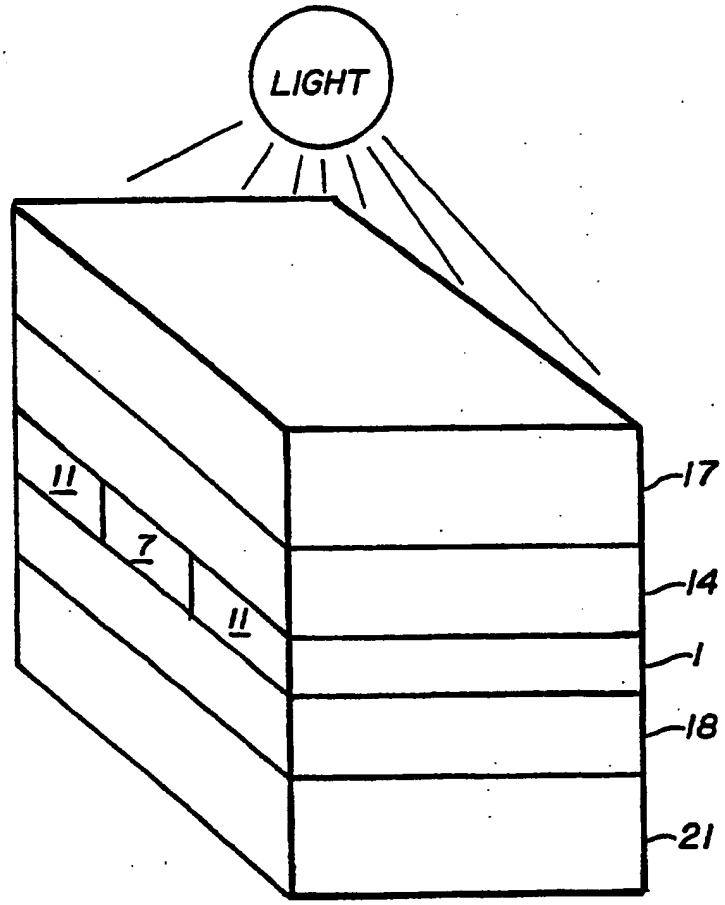


Fig. 9

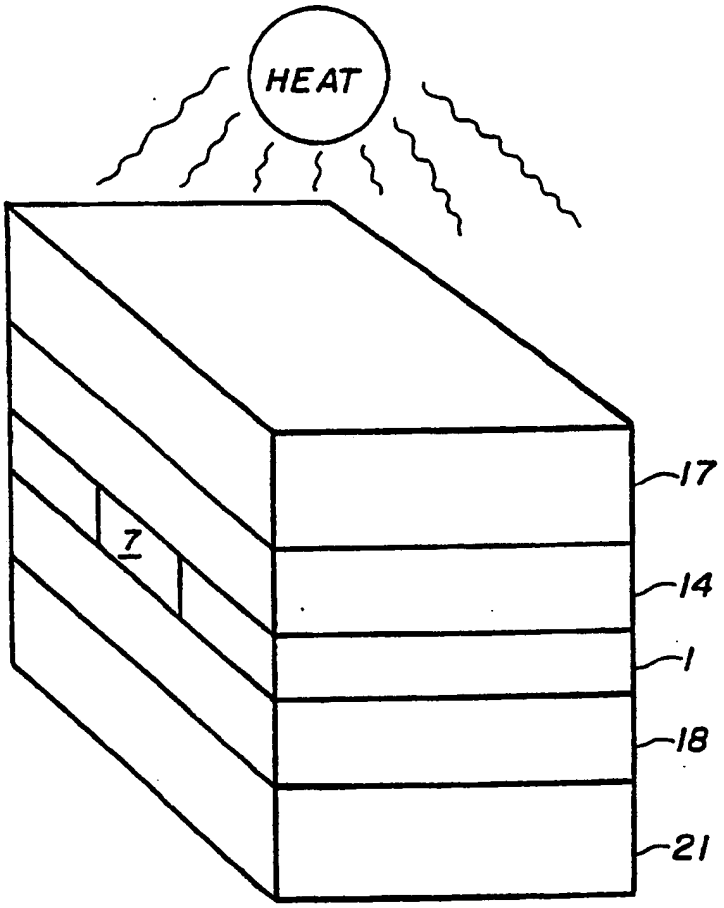


Fig. 10

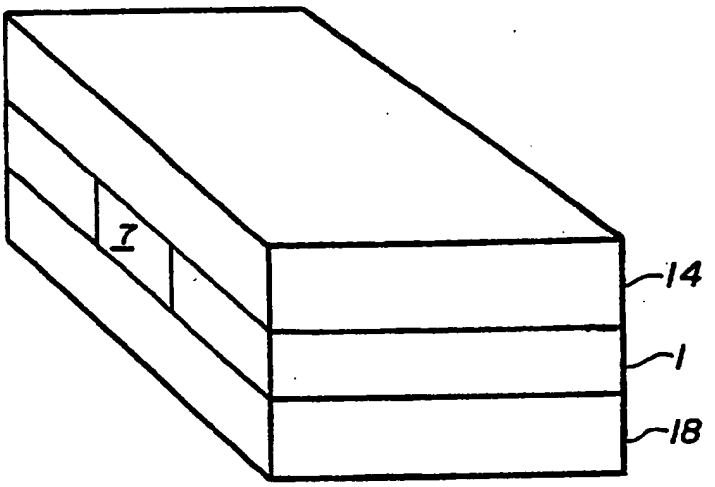
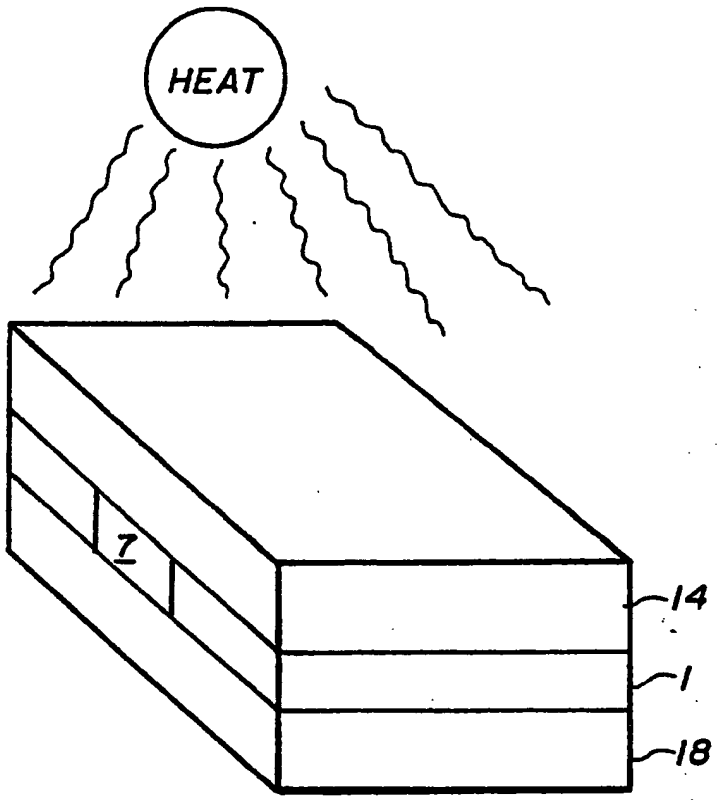


Fig. 11



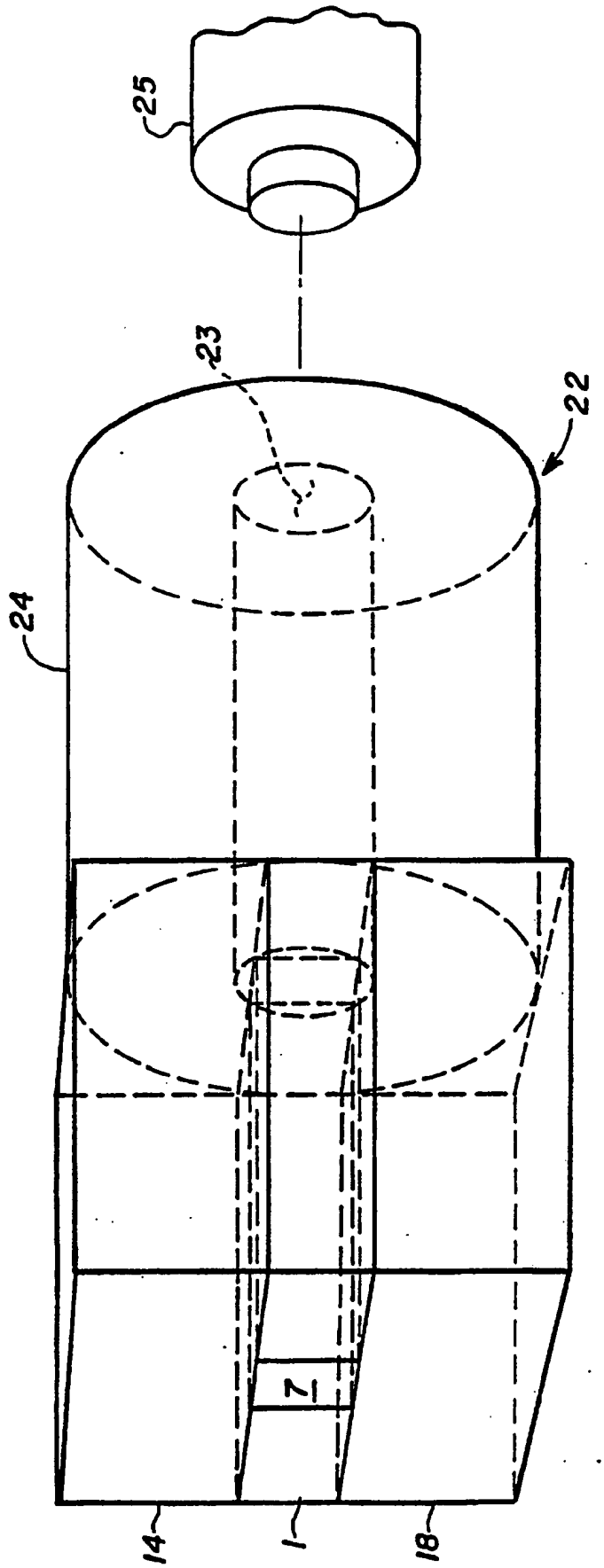


Fig. 12

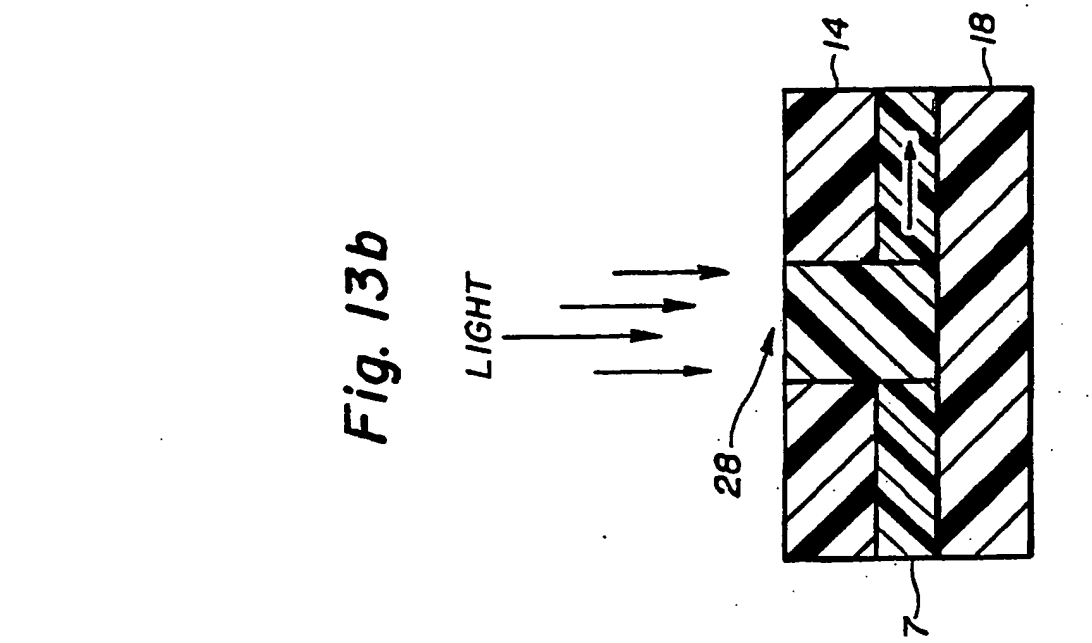


Fig. 13b

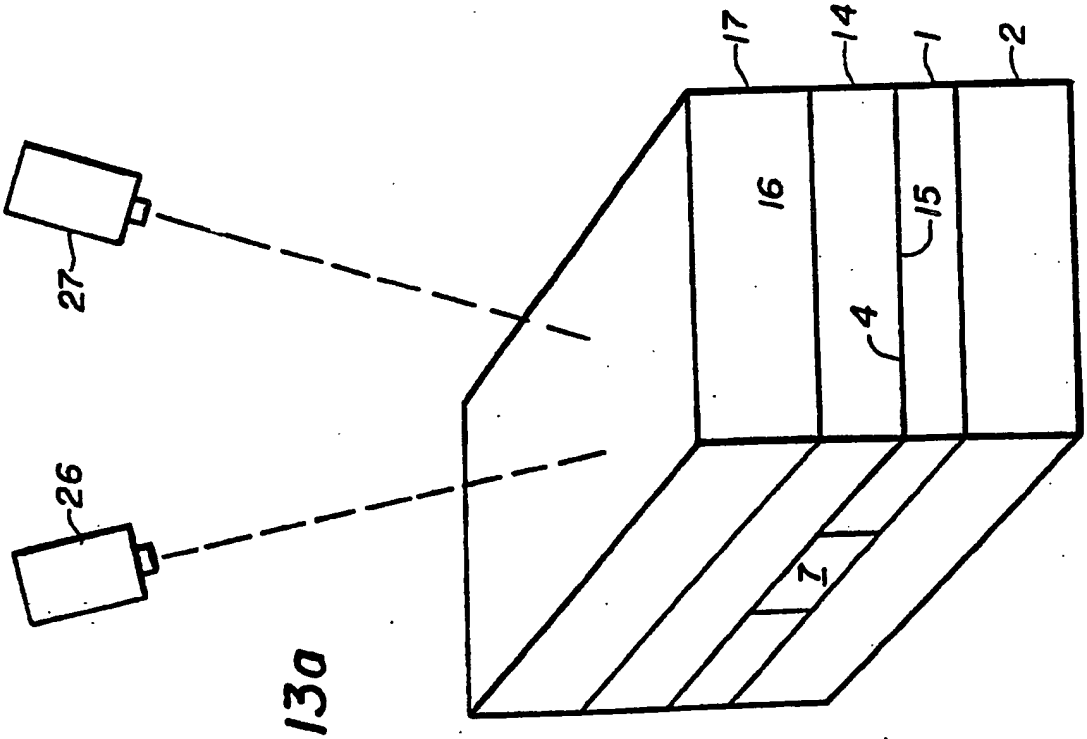


Fig. 13a

Fig. 14

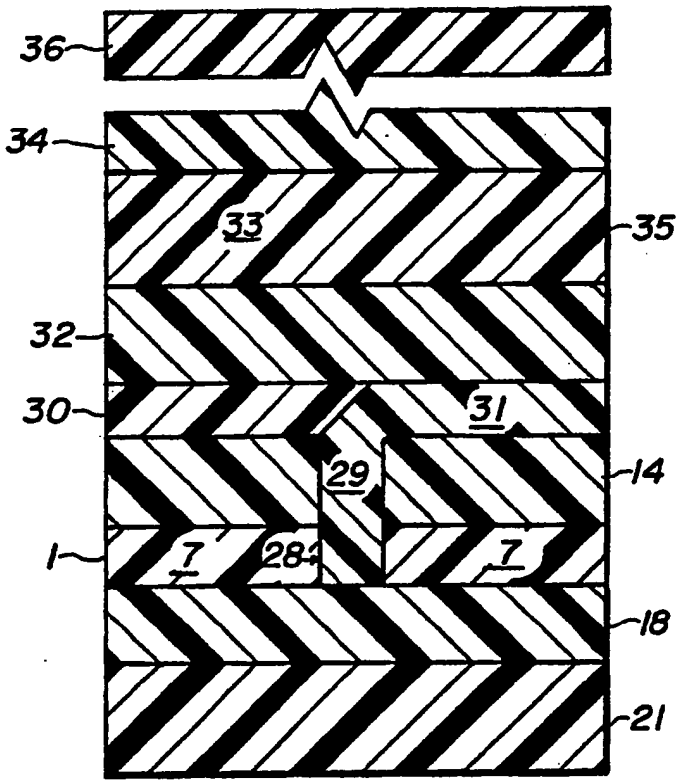


Fig. 15

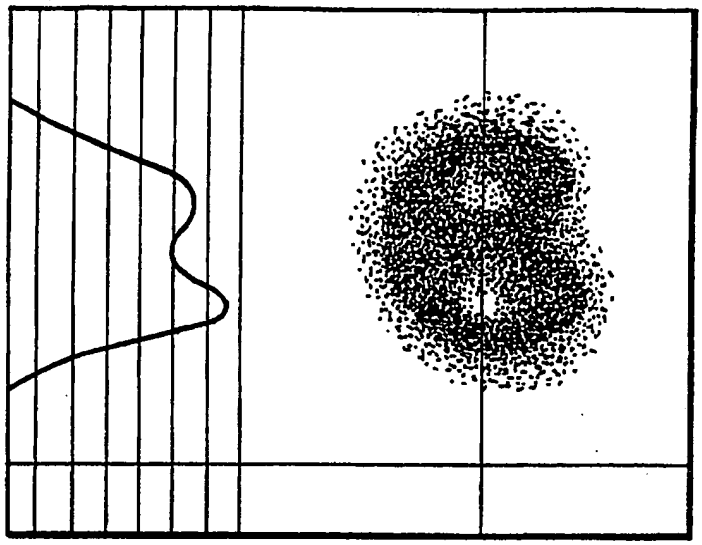


Fig. 16

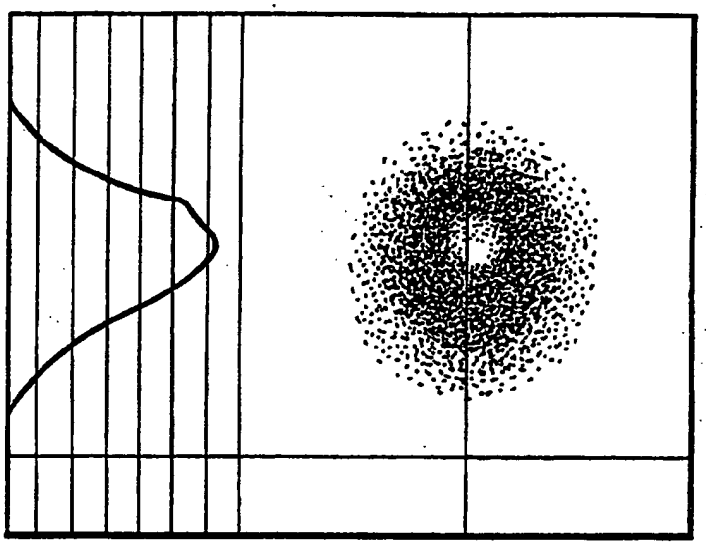
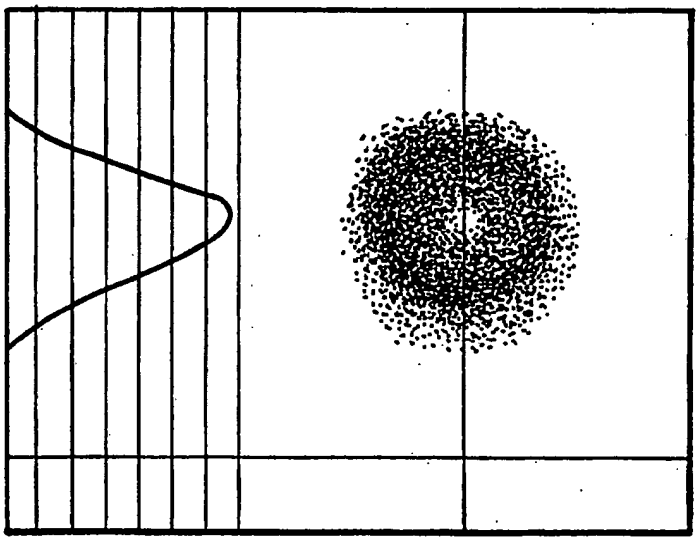


Fig. 17



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/03557

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: G 02 B 6/12

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	G 02 B 6/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 3809732 (E.A. CHANDROSS et al.) 7 May 1974 see column 3, line 15 - column 9, line 34; figures 1-2D (cited in the application) --	1
A	Applied Physics Letters, volume 48, no. 19, 12 May 1986, American Institute of Physics, J.F. Giuliani et al.: "Fabrication of an integrated optical waveguide chemical vapor microsensor by photopolymerizaion of a bifunctional oligomer", pages 1311-1313 The whole article --	1

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13th November 1990	29. 11. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. Peis / M. PEIS

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Electronics & Communications in Japan, volume 65, no. 11, November 1982, Scripta Publishing Co. I. Kato et al.: "Polymer thin film optical waveguide", pages 101-107 see the whole article --	1
A	Patent Abstracts of Japan, volume 11, no. 66 (P-552)(2513), 27 February 1987 & JP, A, 61228403 (HITACHI LTD) 11 October 1986 see the abstract ----	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9003557 SA 39078

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/11/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3809732	07-05-74	None	

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82